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<b>(54) Title:</b> ELASTOMERIC COPOLYMER														
<b>(57) Abstract</b>  <div style="display: flex;"> <div style="flex: 1;"> <p>The invention relates to an elastomeric copolymer comprising 25-85 wt.% of ethylene, 15-75 wt.% of <math>\alpha</math>-olefine and optionally up to 20 wt.% of diene. It is characterized in that the copolymer has a Uniform Branching Coefficient, UBC, which satisfies the relation (a). The invention also relates to a process for the preparation of such an elastomeric copolymer. In this process a catalyst having a reactivity factor <math>RF &lt; 10</math> is used.</p> </div> <div style="flex: 1; text-align: center;"> <math display="block">0.6 \geq UBC = \frac{g' \text{ (III)}}{PD} \geq 0.12 + 8 \cdot 10^{-3} \times \Delta\delta \quad (a)</math> </div> </div>														

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ELASTOMERIC COPOLYMER

5

The invention relates to an elastomeric copolymer comprising 25-85 weight % of ethylene, 15-75 weight % of  $\alpha$ -olefine and optionally up to 20 weight % of diene, as well as to a process for the preparation of such an elastomeric copolymer.

An elastomeric copolymer on the basis of ethylene and an  $\alpha$ -olefine has been known, described and prepared for a long time already. Such a product has rubber-like properties and will here and in the following also be referred to as 'EAM' or 'EADM' (products based on ethylene,  $\alpha$ -olefine and optionally diene).

A special type of such an elastomeric copolymer is EPM or EPDM (products in which the  $\alpha$ -olefine is propylene). Such a copolymer is described for instance in EP-A-44,119.

Elastomeric copolymers can be characterized by means of a number of parameters. Besides the weight percentage of the monomer units there are the molecular weight (expressed as  $M_n$  [the number average molecular weight] or as  $M_w$  [the weight average molecular weight]), the molecular weight distribution or polydispersity PD (defined as  $M_w/M_n$ ), as well as the degree of branching. The degree of branching is determined on the basis of, among other things, a Mark-Houwink relation, which indicates the relation between the molecular weight ( $M$ ) and the intrinsic viscosity  $[\eta]$  of the copolymer. A less linear relation between  $\log [\eta]$  and  $\log M$  indicates an increased degree of branching.

To that end, absolute molecular weight distributions (PDs) of elastomeric copolymers are determined by means of a Size Exclusion Chromatography/Differential Viscometry (SEC-DV) combination, in accordance with the universal calibration principle as

described in: Z. Grubistic, R. Rempp, H. Benoit, J. Polym. Sci., Part B, 5, 753 (1967). It holds that  $\log([\eta] \cdot M)$  vs retention volume = constant,  $[\eta]$  representing the intrinsic viscosity and M the molecular weight. The experimental Mark-Houwink relation yields information on the degree of branching by comparing it with the Mark-Houwink relation for linear polymers, which is used as reference. By 'branching' is understood a ramification in the polymer chain that is longer than a ramification produced by the incorporation of a molecule of the  $\alpha$ -olefine or the diene. The reference Mark-Houwink relation depends on the average ethylene/ $\alpha$ -olefine composition of the polymer. According to Th.G. Scholte, N.L.J. Meijerink, H.M. Schoffeleers, A.M.G. Brands, J. of Appl. Pol. Sci., Vol 29, 3763-3782 (1984), for the Mark-Houwink relation of a linear ethylene-propylene (EP) copolymer it holds that:

$$[\eta]_1 = \left(1 - \frac{1}{3} w_3\right)^{(1+a)} \cdot K_{PE} \cdot M^a$$

where:

- $[\eta]_1$  = intrinsic viscosity of the linear copolymer (in dl/g) having molar mass M;
- $w_3$  = propylene weight fraction;
- $K_{PE}$  = Mark-Houwink constant for linear polyethene (PE) ( $= 4.06 \times 10^{-4}$ , measured in 1,2,4 trichlorobenzene);
- $a$  = Mark-Houwink constant for linear polyolefinic copolymers ( $= 0.725$ , measured in 1,2,4 trichlorobenzene).

$w_3$  for such a copolymer is calculated as:

$$w_3 = C_3 / (C_3 + C_2)$$

where  $C_2$  and  $C_3$  represent the content (in weight percent) of ethylene and propylene, respectively, in the copolymer.

The referenced article also teaches how to use the Mark-Houwink relation for other types of ethylene based copolymers.

The degree of branching can be quantified by the branching  
5 parameter,  $g'$  (III), defined as:

$$g' \text{ (III)} = \{[\eta]_b / [\eta]^*_1\}^{1.725}$$

and wherein:  $[\eta]_b$  is the intrinsic viscosity of the  
10 polymer (in dl/g), and  $[\eta]^*_1$  is the apparent intrinsic viscosity (in dl/g).

The apparent intrinsic viscosity  $[\eta]^*_1$  of a polymer is calculated from the apparent molecular weight distribution, determined via a conventional calibration,  
15 valid for a corresponding linear EP-copolymer with a similar amount of propylene, via the relation:

$$[\eta]^*_1 = (1 - \frac{1}{3} * w_3)^{1.725} * K_{PE} * \frac{\sum [w_i * (M_i^*)^{0.725}]}{\sum w_i}$$

in which:

$w_i$  = weight fraction polymer in SEC elution fraction  $i$   
 $M_i^*$  = apparent molar mass of polymer in SEC elution  
25 fraction  $i$ .

See for this: L.I. Kulin, N.L. Meijerink, P. Starck, Pure & Appl. Chem., vol 60, No. 9, 1403-1415 (1988) and S. Shiga, Polym. Plast. Technol. Eng., 28(1), 17-41 (1989).

The degree of branching can be correlated to the  
30 frequency dependence of the phase angle  $\delta$  from oscillation measurements (Dynamic Mechanical Spectrometry) by means of a rheological experiment,  $\delta$  being the phase difference between the - sinusoidal - shear stress and the resulting shear. These  $\delta$  measurements are carried out at 125°C under  
35 linear viscoelastic conditions. The measurement is described extensively in Kautschuk, Gummi & Kunststoffe, vol. 44 (1991), pp. 128-130; ASTM standard D 4440 is

also referred to. By means of such a measurement the phase angle shift ( $\Delta\delta$ ) is determined, which is the difference in phase angle at  $\log \omega = -1$  and  $\log \omega = +2$ ,  $\omega$  being the oscillation frequency (in rad/s).

5           An increase in branching is normally reflected in a decrease in  $\Delta\delta$ .

Elastomeric copolymers have been found now, and those are the object of the present invention, which had not been known thus far and which show a strongly  
10   deviating rheological behaviour compared with the known copolymers, i.e. products with a different processing characteristic.

The elastomeric copolymer according to the invention is characterized in that the elastomeric  
15   copolymer has no crystallinity above 25°C and has a Uniform Branching Coefficient, UBC, which satisfies the relation:

$$20 \quad 0.6 \geq \text{UBC} = \frac{g' \text{ (III)}}{\text{PD}} \geq 0.12 + 8 * 10^{-3} * \Delta\delta,$$

in which the symbols have the following meaning:

$g' \text{ (III)} = \{[\eta]_b/[\eta]^*_1\}^{1.725}$   
25   PD = polydispersity =  $M_w/M_n$   
 $\Delta\delta$  = phase angle shift during oscillation  
measured at  $\log \omega = -1$  and at  $\log \omega = +2$   
 $\omega$  = oscillation frequency (in rad/s).  
 $[\eta]_b$  = measured intrinsic viscosity (dl/g)  
30    $[\eta]^*_1$  = apparent intrinsic viscosity (dl/g).

The relation between the degree of branching and the molecular weight distribution in such copolymers is completely different from that of the products which have been described and known thus far.

35           Surprisingly, the copolymers according to the invention have a much lower  $\Delta\delta$  value than the value corresponding to the branching characteristic according to

the Mark-Houwink relation for known elastomeric copolymers.

The copolymers according to the invention consist of 25-85 weight % of ethylene, 15-75 weight % of an  $\alpha$ -olefine and optionally up to 20 weight % of diene, i.e. the invention relates to EAM as well as to EADM copolymers. More preferred the ethylene content is between 40 and 70 weight %. In the framework of the present invention the elastomeric copolymers may also comprise more than one  $\alpha$ -olefine and also more than one diene. The polymers exhibit no crystallinity above 25°C, as determined in a DSC measurement (Differential Scanning Calorimetry, in the cooling curve).

The polymers of the present invention preferably are characterized by the following relation:

$$UBC \geq 0.12 + 9 * 10^{-3} * \Delta \delta.$$

Another preferred embodiment is in the following relation:

$$0.6 \geq UBC \geq 0.15 + 9 * 10^{-3} * \Delta \delta.$$

The new copolymers according to the invention can be characterized by substance quantities, known per se, such as molecular weight ( $M_w$  or  $M_n$ ), the polydispersity (PD) and, since they are also of an elastomeric nature, by a Mooney viscosity ( $M_L^{1+4}$ , 125°C). The Mooney viscosity ( $M_L^{1+4}$ , 125°C) is measured according to ISO 289 and is a measure of the plasticity of the product. The copolymer according to the invention has an  $M_w$  of at least 1000; more preferably at least 100,000. Another preference is for a copolymer having a Mooney viscosity ( $M_L^{1+4}$ , 125°C) of at least 20, more preferably at least 35. Such products combine good processability with a good combination of product properties. This applies in particular to products having a PD of between 1.8 and 3.5.

Although not wishing to restrict the invention thereto, it is presently theorized that the branched copolymers of the invention are products whose ramifications are distributed virtually uniformly over all chains of the copolymer, while in conventional products they are mainly associated with the higher molecular weights.

Besides the ethylene, the elastomeric copolymer according to the invention comprises one or more  $\alpha$ -olefines. In general, such an  $\alpha$ -olefine contains 3-25 carbon atoms (although higher  $\alpha$ -olefines are also allowable); more preferably, the  $\alpha$ -olefine contains 3-10 carbon atoms. The  $\alpha$ -olefine has preferably been selected from the group consisting of propylene, butene, isobutene, pentene, 4-methyl pentene, hexene, octene and ( $\alpha$ -methyl) styrene. Most preferably, the  $\alpha$ -olefine is propylene, butene, hexene or octene.

Another possibility is that the elastomeric copolymer comprises a diene, which for instance can have a function in a subsequent vulcanization of the elastomeric copolymer. The diene in the copolymer according to the invention is a polyunsaturated compound; it contains at least two C=C bonds and may be aliphatic as well as alicyclic. Aliphatic polyunsaturated compounds in general contain 3 to 20 carbon atoms, while the double bonds may be conjugated as well as, preferably, non-conjugated. Examples of such compounds are: 1,3-butadiene, isoprene, 2,3-dimethyl butadiene 1,3, 2-ethyl butadiene 1,3, piperylene, mycrene, allene, 1,2-butadiene, 1,4,9-decatrienes, 1,4-hexadiene, 1,5-hexadiene and 4-methyl hexadiene 1,4.

Alicyclic polyunsaturated compounds, with or without a bridging group, may be either monocyclic or polycyclic. Examples of such compounds are norbornadiene and its alkyl derivatives; the alkylidene norbornenes, in particular the 5-alkylidene norbornenes-2, in which the

alkylidene group contains 1 to 20, by preference 1 to 8 carbon atoms; the alkenyl norbornenes, in particular the 5-alkenyl norbornenes-2, in which the alkenyl group contains 2 to 20, by preference 2 to 10 carbon atoms, for instance vinyl norbornene, 5-(2'-methyl-2'-butenyl)-norbornene-2 and 5-(3'-methyl-2'-butenyl)-norbornene-2; dicyclopentadiene and the polyunsaturated compounds of bicyclo-(2,2,1)-heptane, bicyclo-(2,2,2)-octane, bicyclo-(3,2,1)-octane and bicyclo-(3,2,2)-nonane, with at least one of the rings being unsaturated. Further, compounds such as 4,7,8,9-tetrahydroindene and isopropylidene tetrahydroindene can be used. In particular, dicyclopentadiene (DCPD), ethylidene norbornene (ENB), vinyl norbornene (VNB), or hexadiene (HD) are used. Mixtures of the compounds mentioned in the foregoing may also be used.

The diene may be present in the copolymer in quantities of up to 20 weight %, more preferably however up to 10-15 weight %. Even more preferred is an amount of diene in the copolymer of 1-10 weight %, specifically between 2 and 8 weight %.

For various reasons the elastomeric copolymer may contain an amount of extender oil. This oil, of a naphthenic or paraffinnic nature, may be present in quantities of normally up to 250 parts by weight per 100 parts by weight of copolymer. More in particular, 15-150 parts by weight of oil per 100 parts by weight of copolymer are present.

The invention also relates to an elastomer composition, that is to say a compound, of which the elastomeric copolymer constitutes an essential part. Such a compound is made up of components which are required in order to ensure the good properties of the final elastomer preparation. Thus, a compound usually contains one or more of the following components: fillers, carbon black, stabilizers, antioxidants, release agents, vulcanization agents, foaming agents, vulcanization inhibitors and

accelerators, oil. Another possibility is that the elastomer composition comprises a blend of the elastomeric copolymer of the invention and another thermoplastic polymer. Such an other polymer can be a polyolefin (like  
5 polyethylene, polypropylene, polystyrene), a polyamide, a polyester, a polycarbonate and the like. The amount of the elastomeric copolymer in such a blend can be varied, as known by the skilled man, based on the use of such a blend. The blend can be a thermoplastic elastomer as well  
10 as an impact-improved thermoplast. An at least partially vulcanized compound on the basis of the elastomeric copolymer also forms part of the invention. The present invention therefor also relates to thermoplastic elastomers in which the elastomeric copolymer according to the  
15 invention forms an essential part. Preferably the thermoplastic elastomer is at least partially vulcanized, as a result of which a thermoplastic vulcanizate is obtained.

The elastomeric copolymer of the invention can  
20 also be used as additive in lubricating oils, as a result of which another form of elastomer composition is obtained.

The invention also relates to a process for the preparation of the elastomeric copolymer of the invention.  
25 Such a process comprises the polymerization of ethylene and the  $\alpha$ -olefine, optionally in the presence of a diene, under polymerization conditions which are known per se, under the influence of a specific type of catalyst and whether or not in the presence of a cocatalyst. Such a  
30 polymerization can take place in the gas phase as well as in a liquid reaction medium. In the latter case, solution as well as suspension polymerization can be applied. The reaction is preferably carried out continuously, but semi-continuous or batchwise modes of operation are also  
35 possible.

In order to obtain the specific elastomeric

copolymers of the invention a specific type of catalyst is required. The conventional catalysts or catalyst systems (i.e. Ziegler-Natta systems as well as metallocene based catalysts) which have been used thus far are unable to  
 5 yield a product with no crystallinity above 25°C, and which has a UBC as specified in the foregoing.

One of the essential features which such a catalyst must have is a very high reactivity for the  $\alpha$ -olefine. The reactivity can be quantified by means of  
 10 the reactivity factor (RF). The RF indicates the relative affinity of the catalyst for ethylene compared with the  $\alpha$ -olefine. The lower the RF, the lower the preference for ethylene, or the higher the affinity for the  $\alpha$ -olefine. Catalysts that are capable of producing elastomeric  
 15 copolymers according to the invention have an RF < 10, preferably < 6. By nature, RF is always > 0.

The RF of a catalyst can be determined by carrying out a copolymerization of ethylene and an  $\alpha$ -olefine. The RF then  
 20 is the quotient of the ratios between the ethylene and  $\alpha$ -olefine concentrations in the copolymer and the reaction medium, respectively, as expressed in the following formula:

$$\text{RF} = \frac{\frac{[\text{ethylene}]}{[\alpha\text{-olefine}]_{\text{copolymer}}}}{\frac{[\text{ethylene}]}{[\alpha\text{-olefine}]_{\text{reaction medium}}}},$$

determined at an  $\frac{[\text{ethylene}]}{[\alpha\text{-olefine}]_{\text{reaction medium}}} = 0.25$ .

35

All concentrations are in mol%.

An example of a catalyst which meets this requirement is a metallocene catalyst characterized by

'constraint geometry'. Such a catalyst is described for instance in EP-A-416,815, where it is only applied, however, for the preparation of crystalline polyolefine resins having a melting point between 50 and 135°C or a melt index below 125. The elastomeric copolymers according to the invention do not have a melting point or melt index in those ranges; such copolymers or their modes of preparation are not suggested, nor obtained/carried out in said EP-A-416,815. The catalysts described in it, to which explicit reference is made, are only suitable if they have the reactivity factor specified in the foregoing.

Another type of catalyst which can meet the requirements as set forth before regarding the reactivity factors RF is a catalyst having the formula:



- where X is  $(\text{Ar}-\text{R})_s\text{Y}(-\text{R}-\text{DR}'_n)_q$
- and the symbols have the following meanings:
- Me a reduced transition metal from group 4, 5 or 6 of the Periodic Table of the Elements,
  - X a multidentate monoanionic ligand,
  - Y a cyclopentadienyl group, an amidino or phosphidino group, bonded to M,
  - R a connecting group between the Y group and the  $\text{DR}'_n$  or Ar group,
  - D an electron-donating hetero atom chosen from group 15 or 16 of the Periodic Table of the Elements,
  - R' a substituent,
  - Ar an electron-donating aryl group,
  - L a monoanionic ligand bonded to M, to the exclusion of

- a cyclopentadienyl group, an amidino or phosphidino group,
- K a neutral or anionic ligand bonded to M,
- m the number of K groups,
- 5 n the number of R' groups bonded to D,
- q and s  $q + s \geq 1$ .

Some examples of transition metal complexes useful in the process according to the invention are presented in Table 4.

In the following the various components (groups) of such a catalyst will be discussed in more detail.

a) The transition metal (the Me group)

15 The transition metal in the catalyst has been chosen from groups 4-6 of the Periodic Table of the Elements (see the new IUPAC notation to be found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990). More preferably, the transition metal has been chosen from group 4; the highest preference is given to titanium (Ti) as transition metal.

The transition metal is present in reduced form in the catalyst, which means that the transition metal is in a reduced oxidation state. By 'reduced oxidation state' is meant an oxidation state which is lower than the highest possible oxidation state (at most  $Me^{3+}$  for a transition metal of group 4, at most  $Me^{4+}$  for a transition metal of group 5 and at most  $Me^{5+}$  for a transition metal of group 6).

30

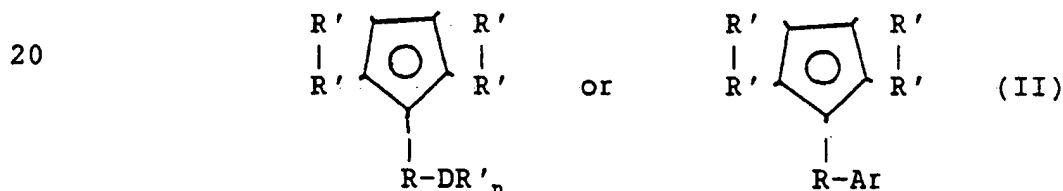
b) The X group

The X group is a multidentate monoanionic ligand consisting of three components: the Y group (a cyclopentadienyl group, an amidino or phosphidino group), the connecting group (bridge) R and the  $DR'_n$  or Ar group (the donor). A multidentate monoanionic ligand is a ligand.

which is bonded covalently to the transition metal at one site (the anionic site, Y) and may be bonded coordinatively to the transition metal at one (bidentate) other site or at several (tridentate, tetradentate, etc.) sites (via the D or Ar group(s)). Examples of tridentate monoanionic ligands are  $Y-R-DR'_{n-1}-R-DR'_n$  and  $Y(-R-DR'_n)_2$ .

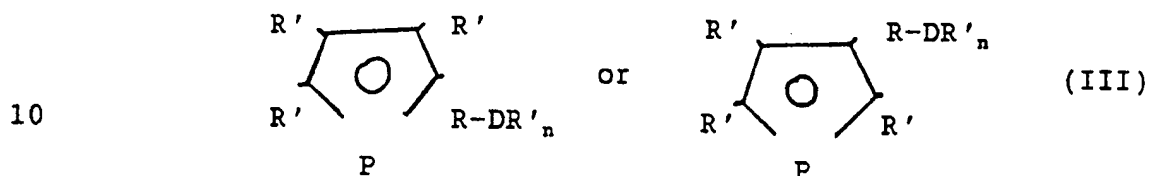
### c) The Y group

The Y group may be a substituted cyclopentadienyl group (Cp group), with the possibility of a substitution in the Y group being present in addition to the substitution at the Y group. One or several of the substituents at the ring is the  $R-DR'_n$  group or the R-Ar group. Examples of an X group with such a Y group (or ligand) have the following structure (with substituents at the ring):



The Cp group may also be a hetero cyclopentadienyl group. Here and in the following a hetero cyclopentadienyl group (in the following also referred to as 'hetero ligand') is understood to be a group that has been derived from a cyclopentadienyl group, but in which at least one of the C atoms in the 5-ring of the cyclopentadienyl has been replaced by a hetero atom, which hetero atom may be chosen from group 14, 15 or 16 of the Periodic Table of the Elements. If there is more than one hetero atom present in the 5-ring of the hetero ligand, these hetero atoms may be either the same or different. More preferably, the hetero atom has been chosen from group 15, while yet more preferably the hetero atom is phosphorus.

By way of illustration of an X group with such a hetero ligand as Cp group, below the structures are represented of two X groups with hetero ligands containing one phosphorus atom as hetero atom (substitution at and in the Y group):



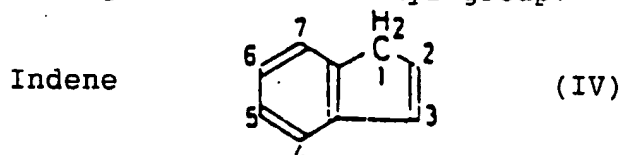
15 For clarity's sake it should be pointed out that the M group as a rule is bonded to the Cp group via an  $\eta^5$  bond. The other R' substituents at the ring of the hetero ligand may be of the same type as those which may be present at the Cp group, as represented in formula (II);

20 the hetero ligand may also be a hetero indenyl, hetero fluorenyl or hetero benzoindenyl group. Preferably, the Cp group according to formula (II) is substituted with four alkyl groups (the Y group is then called a tetraalkyl-cyclopentadienyl group); more preferably, these four alkyl

25 groups are methyl groups.

The numeration of the substitution sites of the indenyl group is in general and in the present description as well based on the IUPAC Nomenclature of Organic Chemistry 1979, rule A 21.1. The numeration of the

30 substituent sites for indene is shown below. This numeration is analogous for an indenyl group:



35 The Y group may also be an amidino ( $-NR'-$ ) or a phosphidino ( $-PR'-$ ) group; in other words, the Y group may

also be a group which contains nitrogen (N) or phosphorus (P) and is bonded covalently to the M group as well as to the R group.

5 d) The R group

The R group, which may also be absent (so that the  $DR'_n$  or Ar group is bonded directly to the Y group (the Cp, amidino or phosphidino group)), constitutes the bond between the Y group and the  $DR'_n$  or Ar group. The  
 10 size of the R group is critical to the extent that it determines the accessibility of the M group relative to the  $DR'_n$  or Ar group, which gives the desired intramolecular coordination. If the R group (or bridge) is too short, the donor may not coordinate well due to ring  
 15 tension. The R groups may each separately be a hydrocarbon group with 1-20 carbon atoms (e.g. alkylidene, arylidene, aryl alkylidene, etc.). Examples of such groups are methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably,  
 20 the R group has the following structure:



where  $p = 1-4$ . The  $R'$  groups may each separately be as  
 25 defined hereafter.

Besides carbon, the main chain of the R group may also contain silicon or germanium. Examples of such R groups are: dialkyl silylene, dialkyl germylene, tetra-alkyl disilylene or tetraalkyl silaethylene ( $-SiR'_2CR'_2-$ ).  
 30 The alkyl groups in such a group preferably have 1-4 carbon atoms and more preferably are a methyl or ethyl group.

e) The  $DR'_n$  group

35 This donor group consists of an electron-donating hetero atom D, chosen from group 15 or 16 of the

Periodic Table of the Elements, and one or more substituents R' bonded to D. The number of R' groups is linked up with the nature of the hetero atom D, in the sense that  $n = 2$  if D is from group 15 and  $n = 1$  if D is  
5 from group 16. The R' substituent bonded to D is as defined hereafter with the exception that it cannot be H.

The hetero atom D has preferably been chosen from the group comprising nitrogen (N), oxygen (O), phosphorus (P) and sulphur (S); more preferably, the  
10 hetero atom is nitrogen (N) or phosphorus (P). It is further possible for two R' groups in the  $DR'_n$  group to be connected with each other to form a ring-shaped structure (so that the  $DR'_n$  group can be a pyrrolidinyl group). The  $DR'_n$  group can form coordinative bonds with M.

15

#### f) The Ar group

The electron-donating group (or donor) used may also be a substituted or non-substituted aryl group ( $C_6R'_5$ ), such as phenyl, tolyl, xylyl, mesitylyl, cumyl,  
20 tetramethyl phenyl, pentamethyl phenyl, etc. The coordination of this Ar group in relation to M may vary from  $\eta^1$  to  $\eta^6$ .

#### g) The R' group

25 The R' groups may each separately be hydrogen or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like). Examples of such hydrocarbon radicals are methyl, ethyl, propyl, butyl, hexyl, decyl, phenyl and the like. Also, two adjacent  
30 hydrocarbon radicals may be connected with each other in a ring system; therefore the Cp group may be an indenyl, a fluorenyl or a benzoindenyl group. Such a group as well may contain one or more R' groups as substituents. R' may also be a substituent which instead of or in addition to  
35 carbon and/or hydrogen may comprise one or more hetero atoms of groups 14-16 of the Periodic Table of the

Elements. Thus, a substituent may be a Si-containing group.

h) the L group

5           The catalyst contains two ligands L, of a monoanionic nature, which are bonded to the transition metal. Examples of such ligands, which may be identical or different, are: a hydrogen atom, a halogen atom, an alkyl, aryl or aralkyl group, an alkoxy or aryloxy group, a group  
10 comprising a hetero atom chosen from group 15 or 16 of the Periodic Table of the Elements, for example:

- a sulphur compound, such as sulphite, sulphate, thiol, sulphinat, thioalkyl,
  - a phosphorus compound, such as phosphite, phosphate.
- 15 Two L groups may also be connected with each other and so form a dianionic bidentate ring system.

These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

20           Preferably, L is a halogenide and/or an alkyl or aryl group; more preferably, a Cl group and/or a C<sub>1</sub>-C<sub>4</sub> alkyl or a benzyl group. Excluded L groups are a Cp group, an amidino group or a phosphidino group (so L cannot be a Y group).

25

i) the K group

The K group is a neutral or anionic ligand bonded to Me; it may also be absent, on the proviso that if K is monoanionic, the following holds for K<sub>m</sub>:

- 30   m = 0 for Me<sup>3+</sup>  
     m = 1 for Me<sup>4+</sup>  
     m = 2 for Me<sup>5+</sup>

The K group may be a ligand as described for the L group or a (substituted) Cp group (C<sub>5</sub>R'<sub>5</sub>), an amido  
35 (NR'<sub>2</sub>) or a phosphido group (PR'<sub>2</sub>). The K group may also be a neutral ligand such as an ether, an amine, a phosphine,

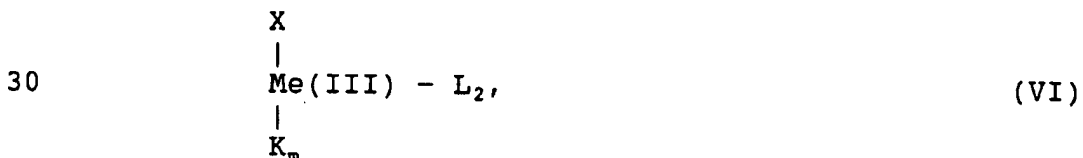
a thioether, etc. Two K groups may also be connected with each other by an R group and so form a bidentate ring system. Thus two K groups may also form together an X group. For each neutral K the value of m is higher by one  
 5 than the value stated above for a monoanionic K group.

As can also be seen from formula (I), the X group of the transition metal consists of a Y group to which are linked one or more donor groups (the Ar groups), linked via an R group, and/or the DR'<sub>n</sub> group(s). The  
 10 number of donor groups is linked closely to the Y group; it is at least 1 and at most equal to the number of substitution sites that are present at a Y group.

With reference, by way of example, to the structure according to formula (II), one (1) substitution  
 15 site in such a Cp group has been taken either by an R-Ar group or by an R-DR'<sub>n</sub> group ( $q + s = 1$ ). If all R' groups in formula (II) are an R-Ar group and/or an R-DR'<sub>n</sub> group, the value of ( $q + s$ ) is 5.

A special embodiment of the catalyst useful in  
 20 the invention comprises a transition metal complex in which a bidentate/monoanionic ligand is present and in which the reduced transition metal has been chosen from group 4 of the Periodic Table of the Elements and has an oxidation state of 3+.

25 In this case the catalyst useful in the invention comprises a transition metal complex of the following structure:



where the symbols have the same meaning as described above  
 35 for formula (I) and where Me(III) is a transition metal chosen from group 4 of the Periodic Table of the Elements and is in oxidation state 3+.

Such a transition metal complex has no anionic K

ligands (for an anionic K,  $m = 0$  in case of  $\text{Me}^{3+}$ ).

A cocatalyst is usually applied in combination with the catalyst. A cocatalyst which may be applied is one on the basis of an organometal compound. The metal in  
5 such an organometal compound has been chosen from groups 1, 2, 12 or 13 of the Periodic System of the Elements. For cocatalysts on the basis of aluminium compounds, see for instance EP-A-287,666, pp. 20-21. Suitable cocatalysts are also benzene-soluble organo-aluminium-oxy compounds as  
10 known from EP-A-360,492. Further see US-A-4,769,428 (column 5), in which organo-aluminium alkyls and linear and cyclic aluminoxanes are used as cocatalyst. Commercial aluminoxanes to be mentioned are methyl aluminoxanes from the producers Witco, Albemarle and Akzo. Preferably,  
15 linear or cyclic aluminoxanes are used as organo-aluminium compound.

In addition to, or instead of the organometal compound, it is also possible to use as cocatalyst a compound which contains or yields in a reaction with the  
20 complex a non-coordinating or loosely coordinating anion. Such compounds have already been described for instance in EP-A-426,637.

The quantity of cocatalyst on a molar basis relative to the quantity of complex usually amounts to  
25 1 : 1 - 10,000 : 1, preferably 1 : 1 - 2,500 : 1 if an organometal compound is used as cocatalyst. If a compound containing or yielding a non-coordinating or loosely coordinating anion is used as cocatalyst, the ratio usually is 1 : 100 - 1,000 : 1, preferably 1 : 2 -  
30 250 : 1.

The catalyst as well as the cocatalyst may be present in the catalyst composition in the form of a single component or as a mixture of several components. This may be the case in particular in those situations  
35 where it is desirable to influence the molecular properties, such as the molecular weight and in particular

the molecular weight distribution.

The catalyst or catalyst composition according to the invention may be applied by a method known as such as a catalyst component for the polymerization to the elastomeric copolymer according to the invention.

In the process according to the invention the catalyst or the catalyst composition may be applied either on a carrier or without a carrier. The supported catalysts are mainly used in gas phase and slurry processes. The carrier used may be any carrier that is known as a catalyst carrier, for instance  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{MgCl}_2$ .

The carrier may be used as such, or be modified, for example by silanes, aluminiumalkyls, aluminoxanes, and others. The catalyst composition may also be prepared by in-situ methods.

Polymerization to the elastomeric copolymer can take place in a known manner, in the gas phase as well as in a liquid reaction medium. In the latter case, both solution and suspension polymerization are suitable, with the quantity of transition metal to be used generally being such that its concentration in the dispersion agent amounts to  $10^{-8}$  -  $10^{-4}$  mol/l, preferably  $10^{-7}$  -  $10^{-3}$  mol/l.

The person skilled in the art is familiar with the dispersion agent to be used in such a process.

The polymerization is generally carried out at temperatures between  $-40^\circ\text{C}$  and  $250^\circ\text{C}$ , more preferably between  $-15^\circ\text{C}$  and  $200^\circ\text{C}$ . Surprisingly it has been found that with catalysts that satisfy the required criterion (a reactivity factor  $\text{RF} < 10$ , preferably  $< 6$ ) the elastomeric copolymers according to the invention can be produced at temperatures higher than the usual temperatures, with maintenance of the polymerization activity. Preferably therefore the polymerization is effected at temperatures between  $35$  and  $180^\circ\text{C}$ .

The pressure will usually amount to  $0.1$ - $50$  MPa, although higher or lower pressures are also practicable.

The person skilled in the art will be very well able to obtain the desired composition of the elastomeric copolymer by adjusting the amounts of the ethylene, the  $\alpha$ -olefine and, where applicable, the diene supplied. This  
5 also applies to adjusting and controlling of the molecular weight or the molecular weight distribution.

Because the catalysts to be used in the process permit the application of an increased polymerization temperature, compared with the state of the art, the  
10 polymerization in solution may also be performed with a higher copolymer concentration in the solution. Preferably, this concentration is between 10 and 45 wt%.

The elastomeric copolymers according to the invention are suitable for a wide variety of applications,  
15 for instance for the manufacture of hoses, cables, conveyor belts, sealing profiles. They can be vulcanized by the customary methods, for instance by means of substances yielding free radicals, such as peroxides, or with sulphur. These copolymers have excellent processing  
20 characteristics. The customary techniques used to make a rubber processable can also be applied to these copolymers.

The invention will be elucidated by means of a few examples and comparative experiments, without being  
25 restricted thereto.

#### Analysis of the elastomeric copolymers.

The elastomeric copolymers that were prepared as described  
30 in the Examples were analyzed by means of Size Exclusion Chromatography/Differential Viscosimetry Combination in accordance with the method described in the foregoing. All copolymers were elastomeric and in a DSC analysis they showed no peaks with a peak temperature higher than 25°C;  
35 most copolymers showed no peaks at temperatures higher than 0°C.

The equipment and the experimental conditions for this SEC-DV analysis were as follows:

Equipment: Waters M150c Gel Permeation  
5 Chromatograph (GPC) with DRI detector,  
used for Size Exclusion Chromatography  
Viscotek Differential Viscometer (DV),  
model 100-02;  
10 Detectors in parallel configuration  
with heated line interface (HLI);  
Erma solvent degasser ERC-3522;  
LiChroma III pump pulse dampener  
(Viscotek) and high-sensitivity  
accessory (Waters);  
15 Data processing: Viscotek data processing software,  
UNICAL 4.04;  
Columns: Toyo Soda (TSK) GMHXL-HT mixed bed  
(4x);  
Calibration: Universal calibration with linear  
20 polyethylene (PE) standards (molecular  
weight 0.4-4000 kg/mol);  
Temperatures: Column oven 140°C;  
Injector compartment 150°C;  
Pump solvent compartment 60°C;  
25 DV oven 150°C;  
SEC conditions: Flow: 1.0 ml/min;  
Injection volume: 0.300 ml;  
Solvent/eluent: Distilled 1,2,4-trichlorobenzene with  
about 1 g/l of Ionol® as stabilizer;  
30 Sample preparation: Dissolving for 4 hours at approx.  
150°C;  
Filtration through 1.2 µm Ag filter;  
Sample concentration approx. 1.0  
mg/ml.

Examples I-II; comparative experiment A; determination of RF-values

400 ml of dry pentamethylheptane (PMH) and cocatalyst were introduced into a 1.5-litre reactor. The  
5 reactor was conditioned at a pressure of 0.8 MPa by passing a propylene-ethylene mixture over it. The propylene:ethylene ratio in the gas feed was 1, resulting in a propylene:ethylene ratio of 4 in the reaction medium.

When the temperature and the off-gas of the  
10 reactor were constant, catalyst and 100 ml of PMH were pumped into the reactor, which caused the polymerisation reaction to start. During the polymerisation the reactor's gas cap was refreshed with a stream of propylene-ethylene (100 nl/hour and 100 nl/hour, respectively).

15 After 10 min reaction time the pressure in the reactor was relieved and the clear solution was drained from the reactor. The polymer was isolated from the solution through evaporation.

A copolymer of ethylene and propylene was obtained. The  
20 results are given in Table 1.

- 23 -

Example/ Comp. Exp.	catalyst	catalyst	cocatalyst	cat ( $\mu$ mol)	cocat ( $\mu$ mol)	pol.temp ( $^{\circ}$ C)	yield (gram)	C3 (mol%)	RF
I	A	$\text{Me}_2\text{SiCp}^*\text{NtBuTiMe}_2$	$\text{B}(\text{C}_6\text{F}_5)_4$	10	20	148	3.7	44	5.1
II	B	$\text{EtCp}^*\text{N}(\text{Bu})_2\text{TiMe}_2$	$\text{B}(\text{C}_6\text{F}_5)_4$	5	30	125	25	48	4.3
A	C	$\text{VOCl}_3$	SEAC	25	300	40	12	20	16

5

Table 1

 $\text{Cp}^*$  = tetramethylcyclopentadienyl

10 Me = methyl

Et = ethyl

Bu = butyl

SEAC = sesquiethylaluminumchloride

 $\text{B}(\text{C}_6\text{F}_5)_4$  = dimethylanilinium pentafluorophenyl borate

Examples II-XV and comparative experiments B-DContinuous polymerization

5           A number of continuous flows of petrol,  
propylene, ethylene and optionally diene, catalyst and  
cocatalyst were supplied to a 1.5-litre reactor. All  
starting materials were freed of oxygen by means of a Cu-  
deoxo catalyst, and of polar components by means of  
10 columns with molecular sieves type 4A. The solution thus  
obtained was removed continuously from the reactor. In a  
flash vessel the catalyst components were deactivated with  
isopropyl alcohol, the monomers were flashed and the  
solution was stabilized with about 1000 ppm of Irganox  
15 1076®. After working up, the polymer was analyzed.

In Examples II-XV, EPDM rubbers were synthesized  
in continuous experiments. Comparative experiments B, C  
and D describe the analysis of EPDM's prepared by means of  
conventional vanadium catalysts, all with an RF = 16: type  
20 K4802 in experiment A, type K4903 in experiment B (all  
Keltan® rubbers from DSM), EPDM in comparative experiment  
C resulted from comparative experiment A.

The polymerization conditions of the continuous  
polymerization of ethylene, propylene and 5-ethylidene  
25 norbornene-2 (ENB) in Examples II-XV are given in Table 2.  
In this Table are stated: the quantities of petrol,  
propylene, ethylene and 5-ethylidene norbornene-2, the  
quantities of catalyst and cocatalyst added, the  
polymerization temperature (poltemp.) and the  
30 polymerization time (poltime). Two different type of  
catalysts were used: catalyst A from Example I, in  
combination with an aluminoxane as cocatalyst: type  
AkzoMMAO3A.

Catalyst B from Example II, the cocatalyst was  
35 dimethylanilinium pentafluorophenyl borate.

The quantities of ethylene and propylene are expressed in

normal litres per hour (nl/h), "normal litre" being a litre at a pressure of 0.1 MPa and a temperature of 25°C.

The results of the continuous polymerizations according to Examples II-XV and the comparative experiments are shown in Table 3. In the Table are stated: the polymer production, expressed in grammes per hour, the composition of the polymer, determined by means of Fourier Transform Infrared Analysis, expressed in weight per cent, the number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ) and the absolute molecular weight distribution (PD), determined by means of SEC-DV, the Mooney viscosity ( $M_L^{1+4}$ , 125°C) of the elastomeric copolymer and the UBC of the elastomeric polymer.

Example	petrol (kg/h)	propylene (nl/h)	ethylene (nl/h)	diene (ml/h)	diene	cat. (mmol/h)	cat type	co-cat (mmol/h)	poltemp (°C)	poltime (min)
II	1.29	71	133	20	ENB	0.132	A	132	86	20
III	1.29	71	133	20	ENB	0.050	A	45	96	20
IV	1.48	63	118	17	ENB	0.040	A	24	87	20
V	1.46	63	118	23	ENB	0.046	A	35	90	20
VI	1.39	85	146	8.5	ENB	0.040	A	40	89	21
VII	1.39	85	146	8.5	ENB	0.040	A	40	87	21
VIII	1.35	130	111	8.5	ENB	0.040	A	40	86	21
IX	1.39	91	138	73	ENB	0.060	A	60	88	21
X	1.25	121	204	145	ENB	0.060	A	60	87	20
XI	1.41	73	149	119	ENB	0.060	A	60	85	21
XII	1.34	100	162	76	DCPD	0.050	A	50	82	21
XIII	1.40	87	134	34 / 7	ENB/VNB	0.056	A	56	75	21
XIV	2.41	227	287	0	-	0.010	B	0.2	125	10
XV	2.32	262	310	0	-	0.004	B	0.2	121	10

Table 2. Experimental conditions.

Example/ comp. exp.	yield (g/h)	%C3 wt%	%diene (wt%)	Mn kg/mol	Mw kg/mol	PD	Mooney 125 °C	Δδ	UBC
II	245	46	4.1	37	100	2.7	20	12	0.30
III	268	45	3.4	87	205	2.4	47	10	0.34
IV	187	42	3.7	120	280	2.3	85	16	0.37
V	220	43	4.2	87	225	2.6	71	14	0.34
VI	254	45	1.1	52	135	2.6	22	18	0.32
VII	258	46	1.0	74	195	2.6	50	14	0.33
VIII	216	58	0.9	82	200	2.5	42	25	0.36
IX	245	41	10	67	175	2.6	35	18	0.29
X	249	35	12	80	200	2.5	57	23	0.32
XI	240	32	16	76	200	2.7	52	17	0.31
XII	223	39	5.7	41	165	4.0	30	5	0.20
XIII	210	46	3.4/0.4	70	270	3.9	74	4	0.21
XIV	500	47	0	42	97	2.3	11	29	0.44
XV	450	44	0	72	160	2.3	41	27	0.44
B	-	47	4.3	85	240	2.8	74	36	0.36
C	-	46	9.0	90	320	3.5	90	24	0.24
D	-	48	4.3	46	215	4.7	34	13	0.15

Table 3. Results of the polymerizations and analysis of the elastomeric copolymers obtained.

Me	L	Y	R	D	R'	K
Ti	Cl	C <sub>5</sub> H <sub>4</sub>	dimethylsilyl	N	methyl	L
Zr	F	C <sub>5</sub> Me <sub>4</sub>	diethylsilyl	P	ethyl	Y-R'
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X
V	I	Fluorenyl	dibutylsilyl	Sb	n-butyl	diethyl ether
Nb	methyl	benzofluorenyl	methylamido	O	n-pentyl	tetrahydrofuran
Ta	methoxy	octahydrofluorenyl	dimethylgermany	S	methoxy	trimethylamine
Cr	ethoxy	C <sub>5</sub> H <sub>3</sub> (N-Bu)	diethylgermany	Se	ethoxy	triethylamine
Mo	hydride	tetrahydroindenyl	diethylpropylene		Cl	trimethylphosphine
W	isopropyl	C <sub>5</sub> H <sub>3</sub> (SiMe <sub>3</sub> )	tetramethyldisiloxane		F	triethylphosphine
	octyl	methylamido	diphenylsilyl		Br	triphenylphosphine
	propoxy	phenylphosphido	tetramethylsilaethylene		I	dimethylsulphide
	phenoxy		methylene		phenoxyl	dimethylalaniline
	benzyl		diethylmethylene		benzyl	
	methylthio		ethylene		H	
			dimethylethylene			
			ethylphosphidino			
			phenylphosphidino			

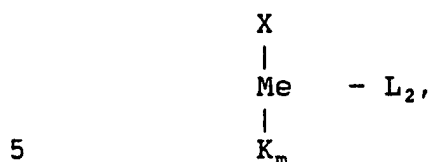
Table 4 Examples of transition metal complexes useful in the invention (see formulas I-VI)

C L A I M S

1. Elastomeric copolymer comprising 25-85 weight % of  
 5 ethylene, 15-75 weight % of  $\alpha$ -olefine and optionally  
 up to 20 weight % of diene, characterized in that the  
 copolymer has no crystallinity above 25°C and has a  
 Uniform Branching Coefficient, UBC, which satisfies  
 the relation:  
 10
 
$$0.6 \geq \text{UBC} = \frac{g' \text{ (III)}}{\text{PD}} \geq 0.12 + 8 * 10^{-3} * \Delta \delta,$$
- 15 in which the symbols have the following meaning:  
 $g' \text{ (III)} = \{[\eta]_b / [\eta]^*_{1}\}^{1.725};$   
 $\text{PD} = \text{polydispersity};$   
 $\Delta \delta = \text{phase angle shift during oscillation, measured at } \log \omega = -1 \text{ and at } \log \omega = +2;$   
 $\omega = \text{oscillation frequency (in rad/s);}$   
 $[\eta]_b = \text{measured intrinsic viscosity (dl/g);}$   
 $[\eta]^*_{1} = \text{apparent intrinsic viscosity (dl/g);}$
2. Elastomeric copolymer according to claim 1,  
 characterized in that the UBC satisfies the relation:  
 25
 
$$\text{UCB} \geq 0.12 + 9 * 10^{-3} * \Delta \delta.$$
3. Elastomeric copolymer according to claim 1,  
 characterized in that the UBC satisfies the relation:  

$$0.6 \geq \text{UBC} \geq 0.15 + 9 * 10^{-3} * \Delta \delta.$$
4. Elastomeric copolymer according to anyone of claims  
 1-3, characterized in that the copolymer has a weight  
 30 average molecular weight of at least 1000.
5. Elastomeric copolymer according to any one of claims  
 1-4, characterized in that the copolymer has a Mooney  
 viscosity ( $M_L^{1+4}$ , 125°C) of at least 20.
- 35 6. Elastomeric copolymer according to any one of claims  
 1-5, characterized in that the copolymer has a Mooney  
 viscosity ( $M_L^{1+4}$ , 125°C) of at least 35.

7. Elastomeric copolymer according to any one of claims 1-6, characterized in that the  $\alpha$ -olefine has been chosen from the group comprising propylene, butene, isobutene, pentene, 4-methyl pentene, hexene, octene, styrene and ( $\alpha$ -methyl-) styrene.
8. Elastomeric copolymer according to any one of claims 1-7, characterized in that the PD of the copolymer has a value between 1.8 and 3.5.
9. Elastomeric copolymer according to any one of claims 1-8, characterized in that the copolymer is based on ethylene, propylene and a diene, the diene having been chosen from the group comprising hexadiene, ethylidene norbornene, vinyl norbornene and dicyclopentadiene.
10. Elastomer composition comprising an elastomeric copolymer according to any one of claims 1-9.
11. Elastomer composition according to claim 10, characterized in that the composition is at least partially vulcanized.
12. Process for the preparation of an elastomeric copolymer according to any one of claims 1-9, characterized in that ethylene and an  $\alpha$ -olefine are polymerized under the influence of a catalyst having a reactivity factor  $RF < 10$ .
13. Process according to claim 12, characterized in that ethylene and an  $\alpha$ -olefine are polymerized under the influence of a catalyst having a reactivity factor  $RF < 6$ .
14. Process according to any one of claims 12-13, characterized in that ethylene and an  $\alpha$ -olefine are polymerized under the influence of a catalyst system comprising a constraint geometry catalyst and a cocatalyst.
15. Process according to any one of claims 12-14, characterized in that a catalyst is used having the formula:



where X is  $(\text{Ar}-\text{R})_s\text{Y}(-\text{R}-\text{DR}'_n)_q$

and the symbols have the following meanings:

- Me a reduced transition metal from group 4, 5 or  
10 6 of the Periodic Table of the Elements,  
X a multidentate monoanionic ligand,  
Y a cyclopentadienyl group, an amidino or  
phosphidino group, bonded to M,  
R a connecting group between the Y group and  
15 the  $\text{DR}'_n$  or Ar group,  
D an electron-donating hetero atom chosen from  
group 15 or 16 of the Periodic Table of the  
Elements,  
R' a substituent,  
20 Ar an electron-donating aryl group,  
L monoanionic ligand bonded to M, to the  
exclusion of a cyclopentadienyl group, an  
amidino or phosphidino group,  
K a neutral or anionic ligand bonded to M,  
25 m the number of K groups,  
n the number of R' groups bonded to D,  
q and s  $q + s \geq 1$ .

16. Process according to any one of claims 12-15,  
characterized in that the polymerization is carried  
30 out at a temperature of  $-15$  to  $200^\circ\text{C}$ .  
17. Process according to claim 16, characterized in that  
the polymerization temperature is between  $35$  and  
 $150^\circ\text{C}$ .  
18. Process according to any one of claims 12-17,  
35 characterized in that the transition metal in the  
catalyst has been chosen from group 4 of the Periodic  
System of the Elements.  
19. Process according to any one of claims 12-18,

characterized in that the polymerization is carried out in solution, the copolymer being present in a concentration of 10-45 wt%.

- 5      20. Object wholly or partly made of an elastomeric copolymer or of an elastomer composition according to any one of claims 1-11 or prepared in accordance with a process of any one of claims 12-19.
- 10      21. Elastomeric copolymer, elastomer composition, process and object as substantially described and further elucidated in the examples.

## INTERNATIONAL SEARCH REPORT

Inter. natl Application No

PCT/NL 96/00261

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F210/18 C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93 08221 A (DOW CHEMICAL CO) 29 April 1993 see the whole document ---	1-21
Y	EP 0 347 129 A (EXXON CHEMICAL PATENTS INC) 20 December 1989 see claims; examples ---	1-21
X	WO 94 13715 A (EXXON CHEMICAL PATENTS INC) 23 June 1994 see page 8, line 25 - page 25, line 15 ---	1-8, 10, 12-19
X	WO 95 05418 A (DOW CHEMICAL CO) 23 February 1995 see page 7, line 7 - page 16, line 28; claims; examples ---	1, 10, 20, 21
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

\* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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